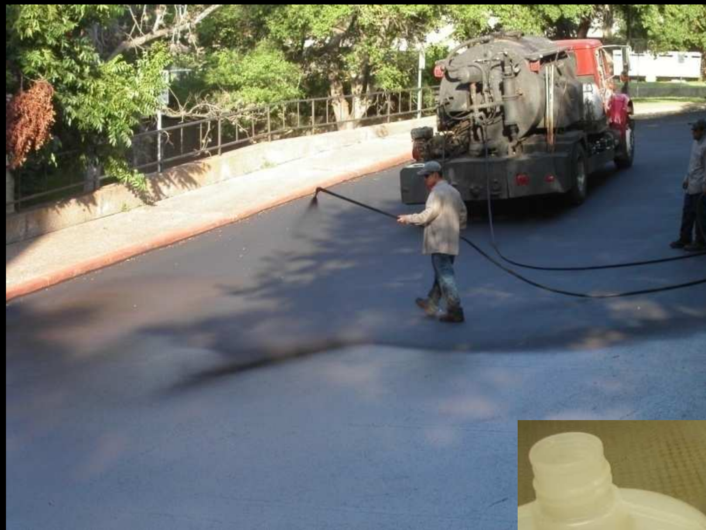


PAHs in the Environment: Trends and Sources

Barbara Mahler and Peter Van Metre

U.S. Geological Survey

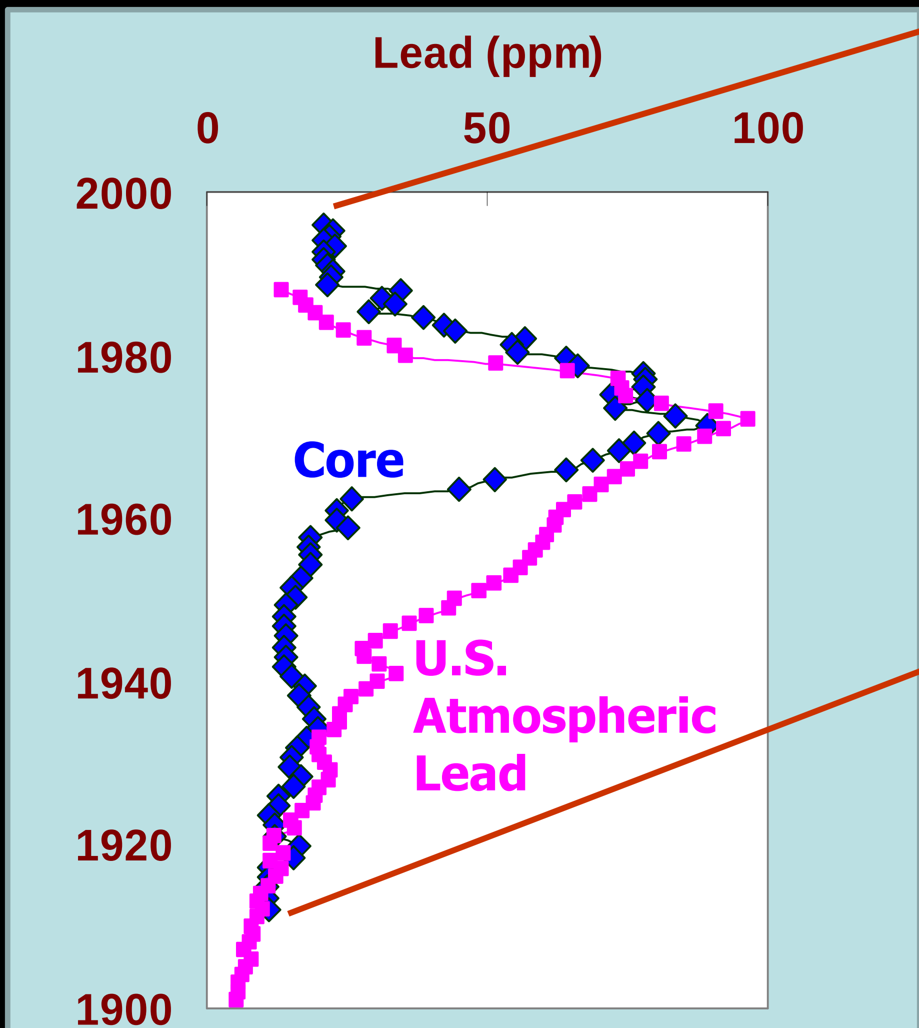
Springfield, Missouri, August 3, 2010

NAWQA – National Water Quality Assessment Program

- **STATUS – characterize water quality nationally**
- **TRENDS – describe trends, or lack of trends**
- **UNDERSTANDING – identify and explain major factors controlling water quality**

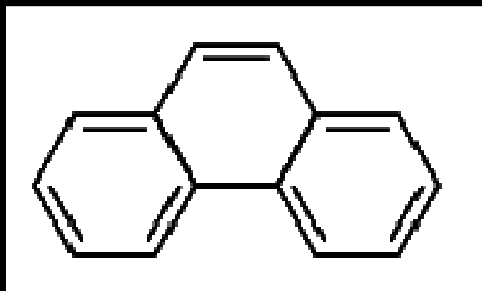
Paleolimnology

If it's persistent and sticks to sediment …

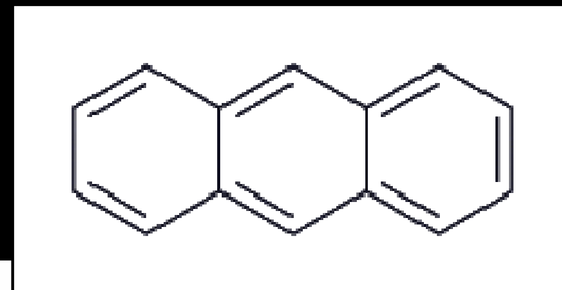


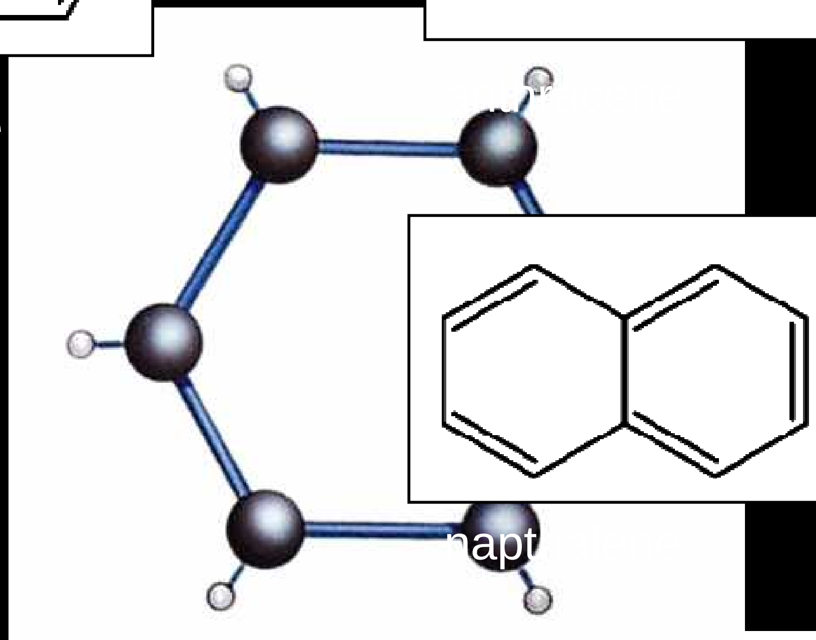
… we can see trends in sediment cores

Chemistry of PAHs

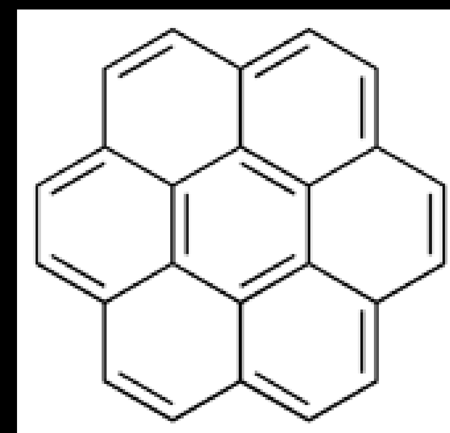


phenanthrene



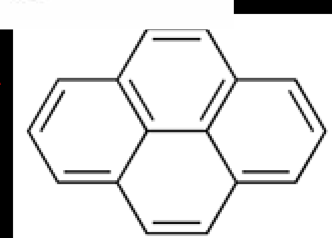


napt



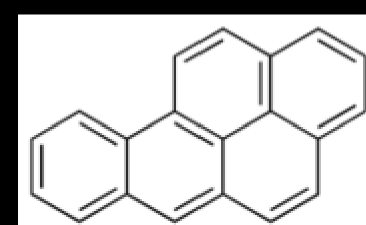
coronene

+



pyrene

=



benzo[*a*]pyrene

Environ. Sci. Technol. 2000, 34, 4064−4070

Urban Sprawl Leaves Its PAH Signature

PETER C. VAN METRE,*[,†]
BARBARA J. MAHLER,[†] AND
EDWARD T. FURLONG[‡]

U.S. Geological Survey, 8027 Exchange Drive, Austin, Texas 78754, and U.S. Geological Survey, P.O. Box 25046, MS 407, Denver Federal Center, Lakewood, Colorado 80225

The increasing vehicle traffic associated with urban sprawl in the United States is frequently linked to degradation of air quality, but its effect on aquatic sediment is less well-recognized. This study evaluates trends in PAHs, a group of contaminants with multiple urban sources, in sediment cores from 10 reservoirs and lakes in six U.S. metropolitan areas. The watersheds chosen represent a range in degree and age of urbanization. Concentrations of PAHs in all 10 reservoirs and lakes increased during the past 20−40 years. PAH contamination of the most recently deposited sediment at all sites exceeded sediment-quality guidelines established by Environment Canada, in some cases by several orders of magnitude. These results add a new chapter to the story told by previous coring studies that reported decreasing concentrations of PAHs after reaching highs in the 1950s. Concurrent with the increase in concentrations is a change in the assemblage of PAHs that indicates the increasing trends are driven by combustion sources. The increase in PAH concentrations tracks closely with increases in automobile use, even in watersheds that have not undergone substantial changes in urban land-use levels since the 1970s.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent the largest class of suspected carcinogens (*1*) and can present a threat to aquatic life (*2*). The presence and distribution of PAHs in the environment are largely a product of the incomplete combustion of petroleum, oil, coal, and wood (*3*). Anthropogenic sources such as vehicles, heating and power plants, industrial processes, and refuse and open burning are considered to be the principal sources to the environment (*4*). On the basis of 1989 data, vehicles produced 11% of PAH emissions in the United Kingdom, domestic coal burning produced 84%, and industrial processes produced 3% (*5*). Several studies in the 1970s and 1980s reported decreasing trends in PAH concentrations in the environment on a regional scale (United States and Europe) since their peak in the 1950s and 1960s (*6*−*9*), on the basis of data from sediment cores from remote and urban lakes and rivers. These reductions have been attributed to reduced use of coal for home heating, industrial emissions controls, and increased efficiency of power plants (*7*, *9*−*11*).

* Corresponding author phone: (512)927-3506; (512)927-3590; e-mail: pcvanmet@usgs.gov.
[†] U.S. Geological Survey, Austin, TX.
[‡] U.S. Geological Survey, Lakewood, CO.

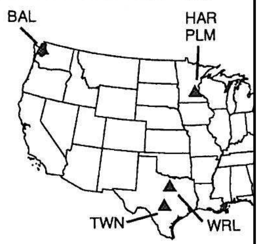


**FIGURE 1. Locations of sampling sites. Al
to lake and reservoir names given in Tab**

While loads of PAHs from som
decreased, the changing face of the
resulted in an increase in another so
use. Growth in the use of land for resid
purposes in the United States now f
population (*12*), a phenomenon te
Increasing sprawl has resulted in dece
and workplace facilities and greater de
as reflected in number of miles travel
vehicle (*13*, *14*). What effect, if any, h
urban water bodies?

As a part of the U.S. Geological S
Quality Assessment (NAWQA) Recor
gram, trends in PAHs were tracked
decades to the mid-to-late 1990s in se
lakes and reservoirs in six U.S. metrop
indicates that trends in PAH concen
watersheds over the last three decade
ing, are increasing and that the incre
the increasing amount of urban spraw
urban and suburban areas.

Methods

Sediment cores from lakes and rese
reconstruct historical trends in water
are recorded for hydrophobic, persist
as PAHs, that bind to sediment pa
particulates and are transported to r
via atmospheric deposition (*17*), sew
surface runoff (*19*). For this study,
collected from seven reservoirs and
United States (Figure 1). Land use in t
reservoirs and lakes is largely mixed
mercial with percent urban land use ra
100% (Table 1). Three sites are in wa
rapid growth since the 1970s (58−12
land use), three sites are in watersheds
growth (26−36%), and four sites ar
relatively stable levels of urban land
of development ranges from the early 1
and Newbridge Pond) to as recently as
Lake).

Cores were collected from the dee
in the lower part of the reservoir and s
discrete subsamples for analysis of [137]
analyzed for selected lakes. Samples
major and minor elements, chlorinat
and PCBs (not presented in this pap

10.1021/es991007n Not subject to U.S. copyrig

Environ. Sci. Technol. 2005, 39, 5567−5574

Trends in Hydrophobic Organic Contaminants in Urban and Reference Lake Sediments across the United States, 1970−2001

PETER C. VAN METRE* AND
BARBARA J. MAHLER

Water Resources Discipline, United States Geological Survey, 8027 Exchange Drive, Austin, Texas 78754-4733

A shift in national policy toward stronger environmental protection began in the United States in about 1970. Conversely, urban land use, population, energy consumption, and vehicle use have increased greatly since then. To assess the effects of these changes on water quality, the U.S. Geological Survey used sediment cores to reconstruct water-quality histories for 38 urban and reference lakes across the United States. Cores were age-dated, and concentration profiles of polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbons were tested statistically. Significant trends in total DDT, *p,p′*-DDE, and total PCBs were all downward. Trends in chlordane were split evenly between upward and downward, and trends in PAHs were mostly upward. Significant trends did not occur in about one-half of cases tested. Concentrations of *p,p′*-DDE, *p,p′*-DDD, and PCBs were about one-half as likely to exceed the probable effect concentration (PEC), a sediment quality guideline, in sediments deposited in the 1990s as in 1965−1975, whereas PAHs were twice as likely to exceed the PEC in the more recently deposited sediments. Concentrations of all contaminants evaluated correlated strongly with urban land use. Upward trends in PAH concentrations, the strong association of PAH with urban settings, and rapid urbanization occurring in the United States suggest that PAHs could surpass chlorinated hydrocarbons in the threat they pose to aquatic biota in urban streams and lakes.

Introduction

Federal environmental policy in the United States changed markedly in about 1970 with the establishment of the U.S. Environmental Protection Agency (1969) and the passage of the Clean Air Act (1970), the Safe Drinking Water Act (1974), the Toxic Substances Control Act (1976), and other laws (*1*). Improving water quality is one objective of these actions. Conversely, increases in population, urban development, energy use, and vehicle use in the United States could lead to degradation of water quality. Identifying water-quality trends can provide measures of the success or failure of mitigation efforts and can provide a warning of unanticipated degradation. Understanding trends also can improve our understanding of cause and effect relations between human activities and water quality and can aid in developing efficient strategies for reducing adverse human effects on the environment.

The U.S. Geological Survey is using paleolimnology, the reconstruction of water-quality histories from age-dated sediment cores, to evaluate water-quality trends across the United States (*2*). Organic compounds that are chemically persistent and strongly hydrophobic often are preserved in the sediments, thus creating a partial record of historical water quality. Downward trends in polychlorinated biphenyls (PCBs) and DDT since the 1960s, for example, have been documented in a variety of environmental settings (*3*, *4*). Trends in chlordane and polycyclic aromatic hydrocarbons (PAHs) have been presented by numerous investigators but are more variable (*5*, *6*). Many studies have addressed trends in these hydrophobic organic compounds (HOCs); however, most are local in scale or focus on only a few water bodies in one region (e.g., *3*−*5*, *7*−*9*).

This study determined trends in persistent HOCs since 1970 using sediment cores collected from 38 lakes across the United States. The study was conducted by the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program (*10*). The primary objectives were to identify trends in HOCs in urban and undeveloped reference settings across the U.S. and, to the extent possible, to determine the causes of those trends. To our knowledge, this study is the first attempt to apply a consistent paleolimnological approach to identifying trends in numerous HOCs across the United States.

Experimental Section

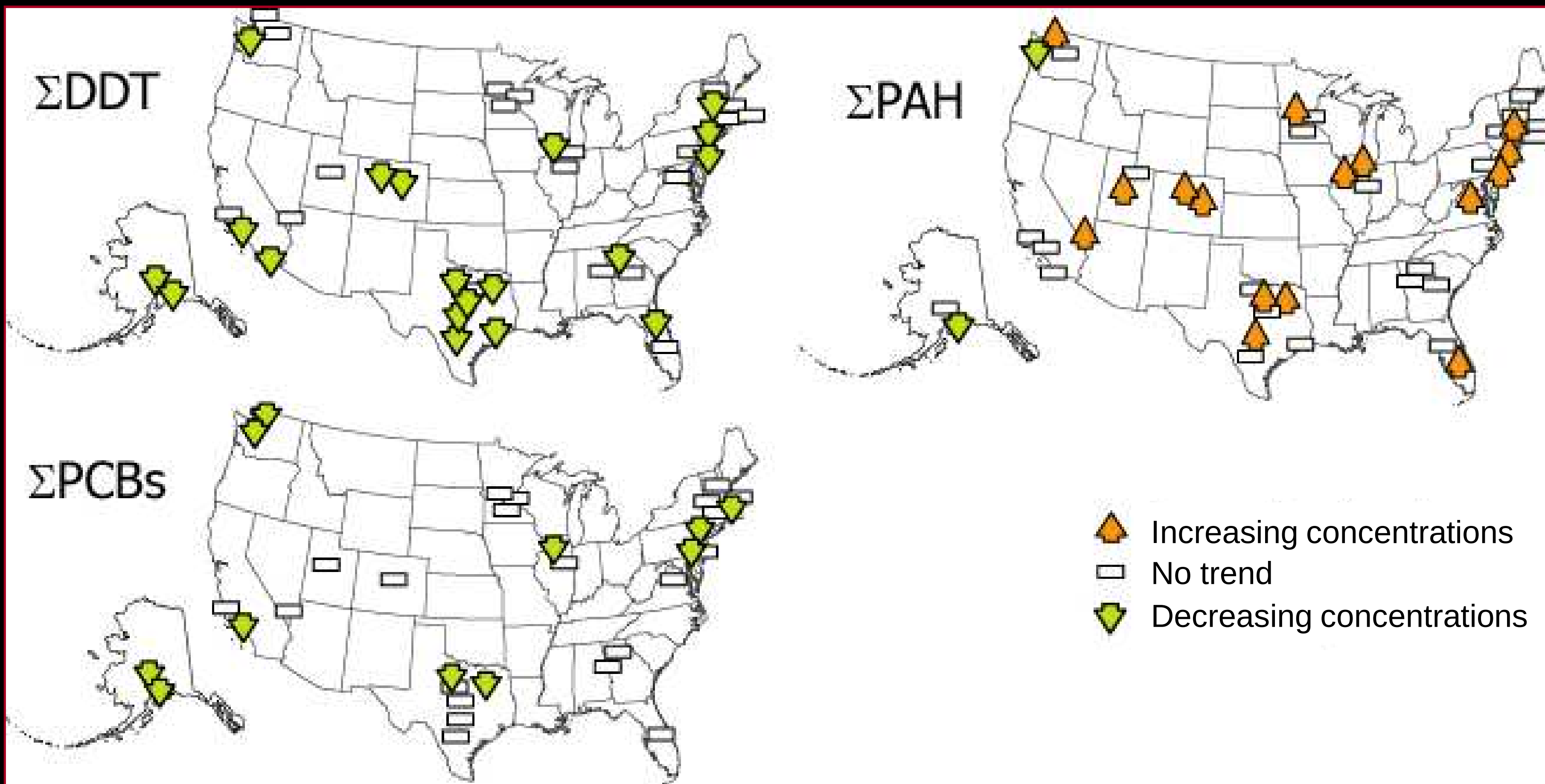
Study Design. Sediment cores were collected from 38 lakes in the United States between 1996 and 2001 (28 reservoirs and 10 natural lakes, hereafter referred to as lakes except where the distinction is relevant), age dated, analyzed chemically, and tested for trends (Figure 1; see Supporting Information for more information on lakes sampled). The NAWQA design provided a national framework for identifying potential study areas (*10*). The selection of urban areas in this study was based on the combination of NAWQA study units, metropolitan statistical areas (MSAs) (*11*), and ecoregions (*12*). Urban areas were selected to represent a diversity of ecoregions where a majority of United States cities and urban populations are located. Lakes in one or more cities in the five most populous (summing urban population only) level II ecoregions and eight of the 11 most populous ecoregions were sampled. In some cases, areas were chosen for study in less populous ecoregions to better represent the geographic diversity of the country (e.g., Las Vegas, NV (Lake Mead) in the Southern Basin and Range was included and Detroit, MI in the Erie/Ontario Lake Plain was not). Although it is not a probabilistic design, it does provide a geographically diverse coverage of major urban areas of the country.

Lakes were chosen for sampling on the basis of lake and watershed size, age of the lake (∼40 years or more for reservoirs), and the amount and age of development in the watershed. The majority of lakes sampled have relatively small watersheds (74% of the watersheds are less than 100 km^2), although drainage area to lake surface area ratios (DA:SA) varied greatly, with generally larger ratios for urban lakes and smaller ratios for reference lakes. This bias was by design, with an objective in sampling the urban lakes being to represent historical trends in anthropogenic inputs to urban streams and an objective in the reference lakes being to represent historical trends in atmospheric deposition. Contaminant inputs to lakes with large DA:SA ratios and development in the watershed are typically dominated by fluvial inputs of contaminants from one or a few streams (*13*, *14*). Lakes with small DA:SA ratios often have contaminant

* Corresponding author phone: (512)927-3506; fax: (512)927-3590; e-mail: pcvanmet@usgs.gov.

10.1021/es0503175 Not subject to U.S. Copyright. Publ. 2005 Am. Chem. Soc.
Published on Web 06/22/2005

Upward trends in PAHs



Van Metre and Mahler, 2005, Environmental Sci. & Tech.

City of Austin monitors stream-bed sediment

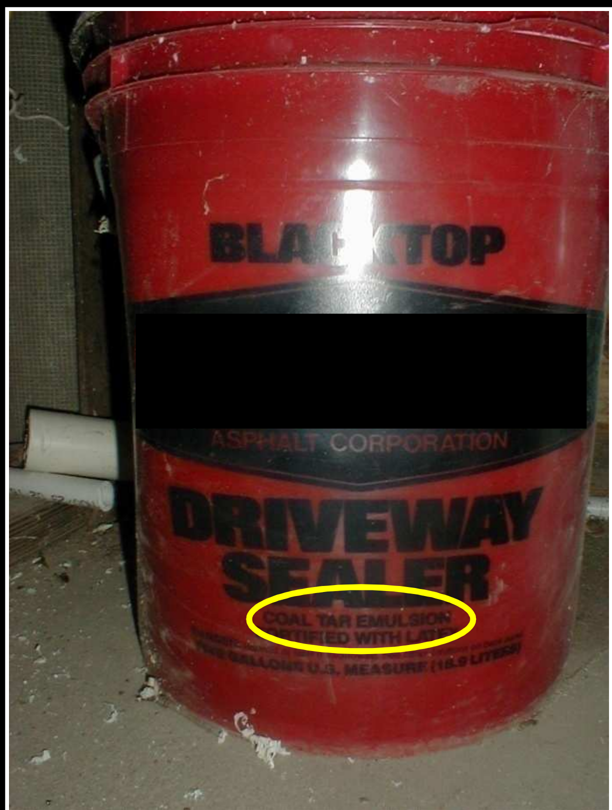
- Extremely high (>1,500 mg/kg) PAHs in some small drainages
- Compare to Probable Effect Concentration (PEC) of 23 mg/kg

What are sources of PAHs?

Sources of PAH: concentrations (mg/kg)

- Tire wear particles
  - **175** (av of 3 studies)
- Road dust
  - **59**
- Brake lining particles
  - **9**
- Air particles, major roadway
  - **104**
- Fresh asphalt
  - **2**
- Weathered asphalt
  - **9**
- Fresh motor oil
  - **7**
- Used motor oil
  - **726**
- Diesel engine particles
  - **17.5**
- Gasoline engine particles
  - **35**
- Coal-tar-based pavement sealcoat (average of 4 products)
  - **92,000**

Coal-tar sealcoat



=

Used motor oil

Clearing up the Confusion

- Coal-tar-based pavement sealer is made from high temperature coal-tar pitch.
- High temperature coal-tar pitch goes by many different names: Road Tar Emulsion Base, Road Tar, Refined Tar, RT-12 Emulsion Tar, Coal Tar Pitch, Pavement Sealer Base and RT-12.

International Chemical Safety Cards

COAL-TAR PITCH

ICSC: 1415

UNEP

National Institute for Occupational Safety and Health NIOSH

Pitch

ICSC # 1415
CAS # 65996-93-2
RTECS # GF8655000
EC # 648-055-00-5
July 03, 2002 Validated
Pi, Study (1st batch of chemical part)

CAS # 65996-93-2 = coal-tar pitch

TYPES OF HAZARD/ EXPOSURE	ACUTE HAZARDS/ SYMPTOMS	PREVENTION	FIRST AID/ FIRE FIGHTING
FIRE	Combustible.	NO open flames.	Foam, dry powder, carbon dioxide.
EXPLOSION			
EXPOSURE		AVOID ALL CONTACT! PREVENT DISPERSION OF DUST!	
•INHALATION	Sneezing. Cough. See EFFECTS OF LONG-TERM OR REPEATED EXPOSURE.	Closed system and ventilation.	Fresh air, rest.
•SKIN	MAY BE ABSORBED! Redness. Burning sensation.	Protective gloves. Protective clothing.	Rinse and then wash skin with water and soap.
•EYES	Redness. Pain.	Safety goggles, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
•INGESTION	See EFFECTS OF LONG-TERM OR REPEATED EXPOSURE.	Do not eat, drink, or smoke during work. Wash hands before eating.	Give plenty of water to drink. Refer for medical attention.

SPILLAGE DISPOSAL	STORAGE	PACKAGING & LABELLING
Sweep spilled substance into sealable containers. Carefully collect remainder, then remove to safe place. Do NOT let this chemical enter the environment. (Extra personal protection: A/P2 filter respirator for organic vapour and harmful dust.)	Separated from strong oxidants. Separated from food and feedstuffs .	Do not transport with food and feedstuffs. Note: H T symbol R: 45 S: 53-45

SEE IMPORTANT INFORMATION ON BACK

ICSC: 1415

Prepared in the context of cooperation between the International Programme on Chemical Safety & the Commission of the European Communities (C) IPCS CEC 1994. No modifications to the International version have been made except to add the OSHA PELs, NIOSH RELs and NIOSH IDLH values.

International Chemical Safety Cards

[redacted]

MATERIAL SAFETY DATA SHEET

Manufacturer:
[redacted]

Emergency Phone No [redacted]
Information Phone No
Date Of Preparation July 18, 1996
Date Supersedes April 19, 1994

SECTION I- IDENTIFICATION

Product Name: **STAR SEAL** - ASPHALT PAVEMENT SEALER

Chemical Family - Refined Coal Tar Pitch Emulsion
Chemical Name - Proprietary.
Prepared by [redacted]

H.M.I.S
Health = 1
Fire = 1
Reactivity = 1

SECTION II- INGREDIENTS

Ingredients	CAS NO.	WT%	Exposure Limits OSHA PEL	ACGIH TLV
Hazardous Ingredients				
Coal Tar Pitch	65996-93-2	29-32	0.2 mg/m3 (Volatiles)	0.2 mg/m3 (Volatiles)
Listed in SARA Title III, Section 313- No.				
STEL	- N/A*			
LC 50	- N/A			
LD 50	- N/A			
Other Ingredients				
Clay	1332-58-7	18-20	N/A	10mg/m3 (dust)
STEL	- 5 MG/M3 (DUST)			
LC 50	- N/A			
LD 50	- N/A			
Water	7732-18-5	48-50	N/A	N/A
Listed in SARA Title III, Section 313 - No.				
STEL	- N/A			
LC 50	- N/A			
LD 50	- CTI OVER 320,000			

* N/A = NOT AVAILABLE OR APPLICABLE

Total weight percentage of all the listed ingredients could be below 100, indicating other unlisted ingredients that are not considered hazardous by any federal (OSHA, WHMIS, SARA), any state or province or local Right-To-Know Regulations.

MATERIAL SAFETY DATA SHEET

Date last revised: 10-01-93

Doc Code: MSDSGSFD

I. General Information

Chemical Name & Synonyms
Dispersion of refined coal tar and mineral fillers in water.

Trade Name & Synonyms
[redacted] "federal" "concentrate"

Hazardous Materials Identification System (HMIS)

HEALTH	FLAMMABILITY	REACTIVITY	PERSONAL PROTECTION
2	0	0	C

Proper DOT Shipping Name
None

DOT Hazard Classification
None

Manufacturer
[redacted]

Manufacturer's Phone #
[redacted]

[redacted]

II. Hazardous Ingredients

Ingredient	*CAS NO.*	*Percent*	*Exposure Limit*
Refined Coal Tar	65996-93-2	31 - 34	0.2 mg/m^3 OSHA PEL Coal tar volatiles benzene soluble fraction 8 hr work shift avg.

III. Physical Data

Boiling Point (^{O}F)
IBP 212^{O}F

Specific Gravity (H_2O=1)
1.2

Vapor Pressure (mm HG.)
Not Determined

Percent Volatile by Volume
Not Determined

Vapor Density (Air =1)
>1

Evaporation Rate (butyl acetate=1)
<1

Solubility in Water
Dispersible, not soluble.

pH
7.4

Appearance & Odor
Viscous brown black liquid with musky coal tar smell.

IV. Fire & Explosion Hazard Data

Flash Point (Test Method)
greater than 140°F (PMCC)

Auto Ignition Temperature
Not determined

Note: Product is a aqueous dispersion and does not support combustion.

Flammable Limits
Not Applicable.

LEL *UEL*

Extinguishing Media
Water, chemical foam, CO_2, or dry chemical for dried film.

Special Fire Fighting Procedures

[redacted]

[Home] [Products] [MSDS] [Contact Us]

MATERIAL SAFETY DATA SHEET
Date Prepared: 03/16/2000
[redacted]

---

1. Chemical Product and Company Identification

Product Identifier: [redacted]
Manufacturer

[redacted]

Emergency Telephone Numbers
[redacted]
Emergency Phone:
1-800-543-7077

---

2. Composition/Information on Ingredients

COMPONENT	CAS#	% BY WT	TLV
Refined Coal Tar	65996-93-2	< 34	0.2 mg/m^3*
Ball Clay	1332-58-7	< 30	0.1 mg/m^3

* TWA, coal tar volatiles benzene soluble fraction, OSHA PEL
** Respirable Crystalline Quartz

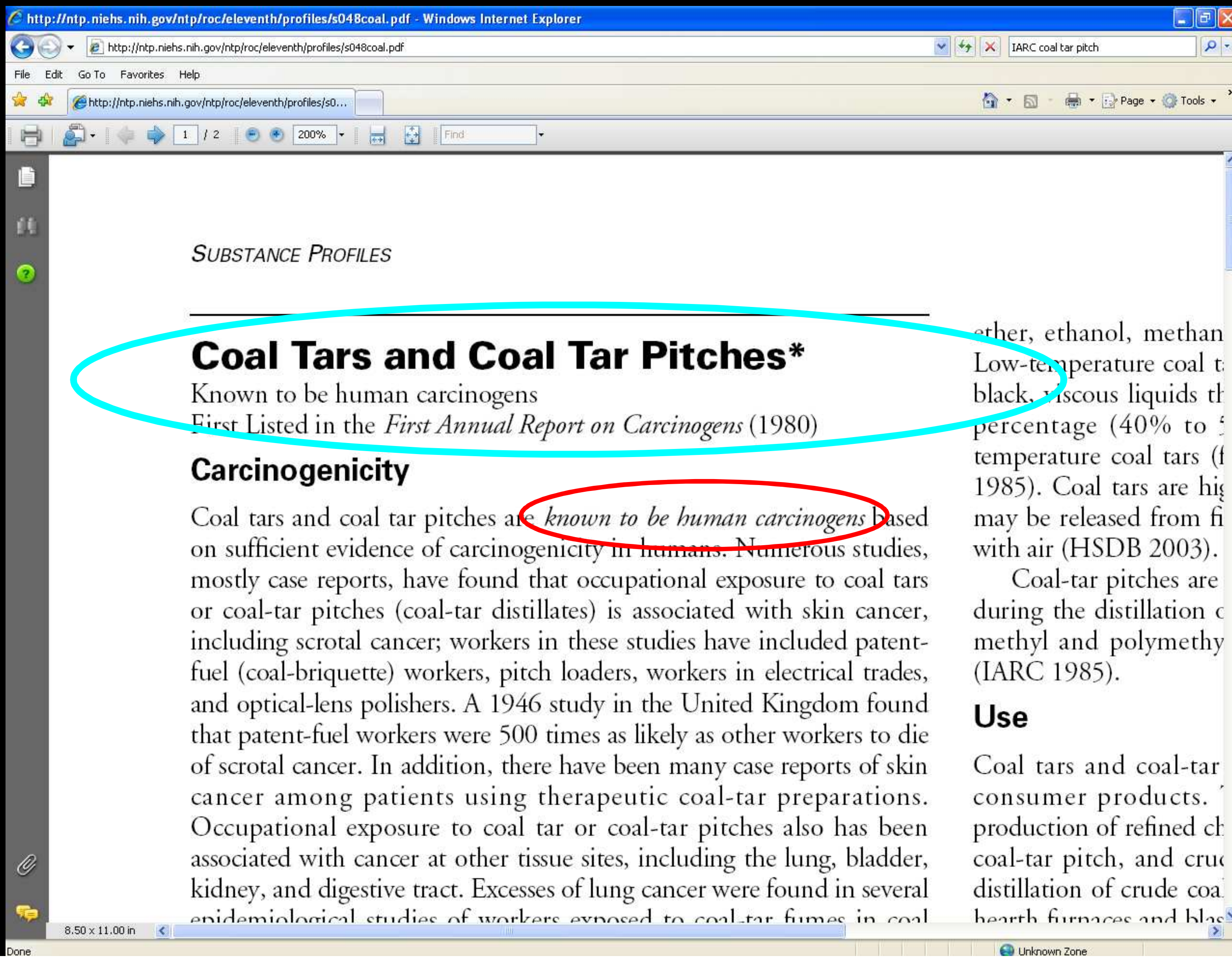
---

3. Hazards Identification

Emergency Overview

Immediate concerns: Studies by Koppers Industries, Inc. (Using Refined Coal Tar Emulsion Safely, 1991) show that emissions during manufacture and application of coal tar emulsion are well below OSHA exposure limits. Avoid prolonged and repeated skin contact. Dermatitis may result from exposure of individuals with sensitive skin. Refined coal tar is a collection of organic compounds, primarily polynuclear aromatic hydrocarbons ranging from one ringed to 30 or 40 ringed in size. It is estimated that as many as 5,000 compounds may be present. Some of these polynuclear aromatic

Coal-tar pitch (by any name) is classified as a known human carcinogen



SUBSTANCE PROFILES

Coal Tars and Coal Tar Pitches*

Known to be human carcinogens

First Listed in the *First Annual Report on Carcinogens* (1980)

Carcinogenicity

Coal tars and coal tar pitches are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans. Numerous studies, mostly case reports, have found that occupational exposure to coal tars or coal-tar pitches (coal-tar distillates) is associated with skin cancer, including scrotal cancer; workers in these studies have included patent-fuel (coal-briquette) workers, pitch loaders, workers in electrical trades, and optical-lens polishers. A 1946 study in the United Kingdom found that patent-fuel workers were 500 times as likely as other workers to die of scrotal cancer. In addition, there have been many case reports of skin cancer among patients using therapeutic coal-tar preparations. Occupational exposure to coal tar or coal-tar pitches also has been associated with cancer at other tissue sites, including the lung, bladder, kidney, and digestive tract. Excesses of lung cancer were found in several epidemiological studies of workers exposed to coal-tar fumes in coal

ether, ethanol, methan
Low-temperature coal t
black, viscous liquids th
percentage (40% to 5
temperature coal tars (f
1985). Coal tars are hig
may be released from fi
with air (HSDB 2003).

Coal-tar pitches are
during the distillation c
methyl and polymethy
(IARC 1985).

Use

Coal tars and coal-tar
consumer products.
production of refined ch
coal-tar pitch, and cruc
distillation of crude coa
hearth furnaces and blas

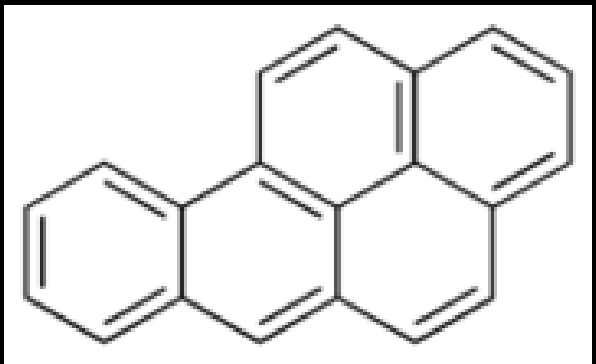
International Agency for Research on Cancer, Report on Carcinogens 11th Edition

What is the difference between crude coal tar and “refined” coal tar?

- The **fractional distillation** of crude coal tar yields light oil, middle oil, heavy oil, and anthracene oil; the **residue is called pitch**.
- On further distillation a large number of substances are obtained, about 200 of which have been isolated. They are used as dyes and in medicines. [Hutchinson Encyclopaedia]

The facts on benzo[*a*]pyrene and other B2 (carcinogenic) PAHs

- Coal-tar sealcoat products contain about 0.5% BaP (average of four products)
- One of 7 PAHs classified as probable human carcinogens ("B2 PAH")



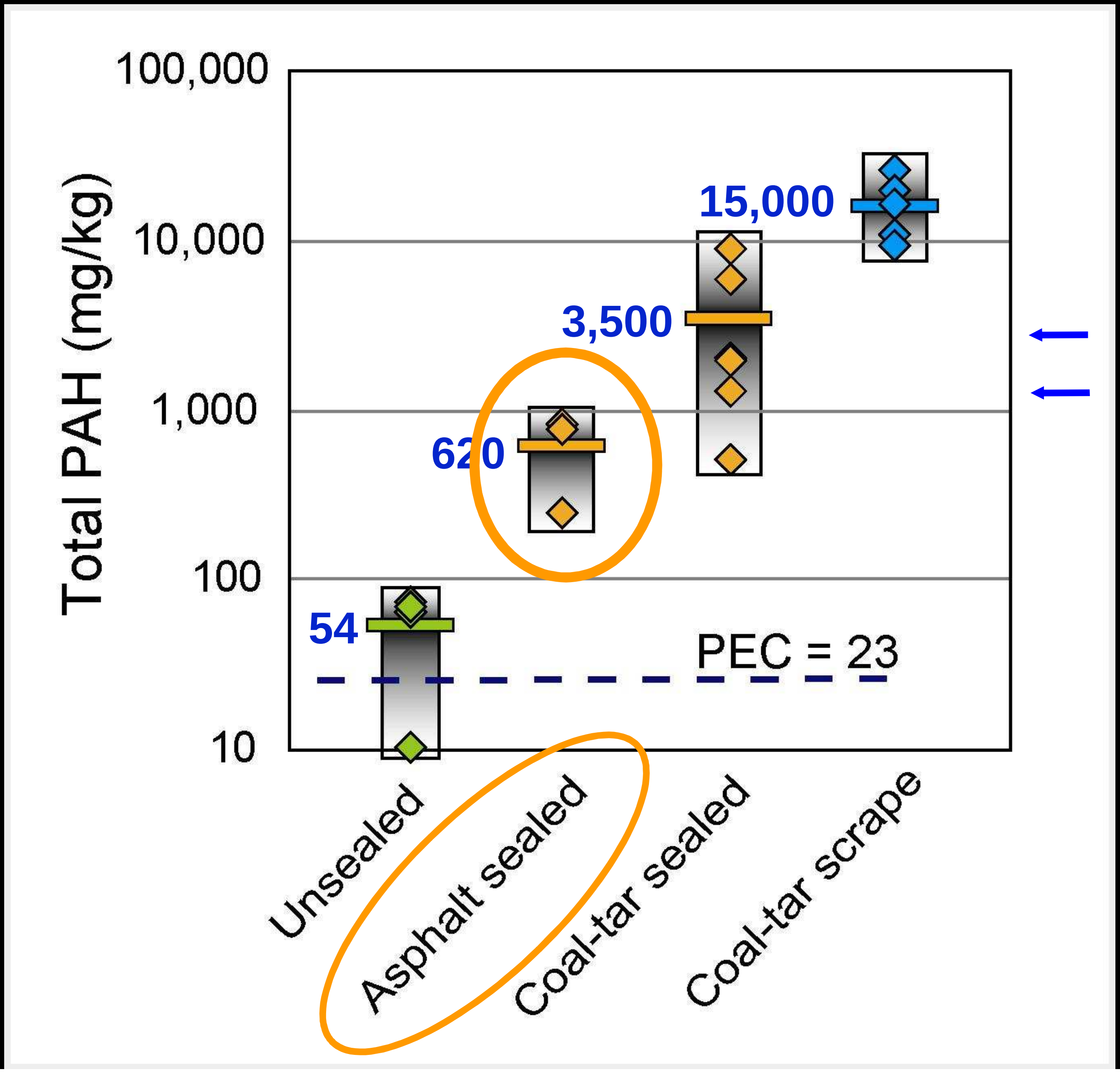
benzo[*a*]pyrene

benzo[*a*]pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenzo[*a,h*]anthracene, and indeno[1,2,3-*cd*]pyrene

USGS - COA Joint Study

- Sample runoff from 13 parking lots
- Analyzed particles and water for PAHs

PAHs in Parking Lot Runoff Particles

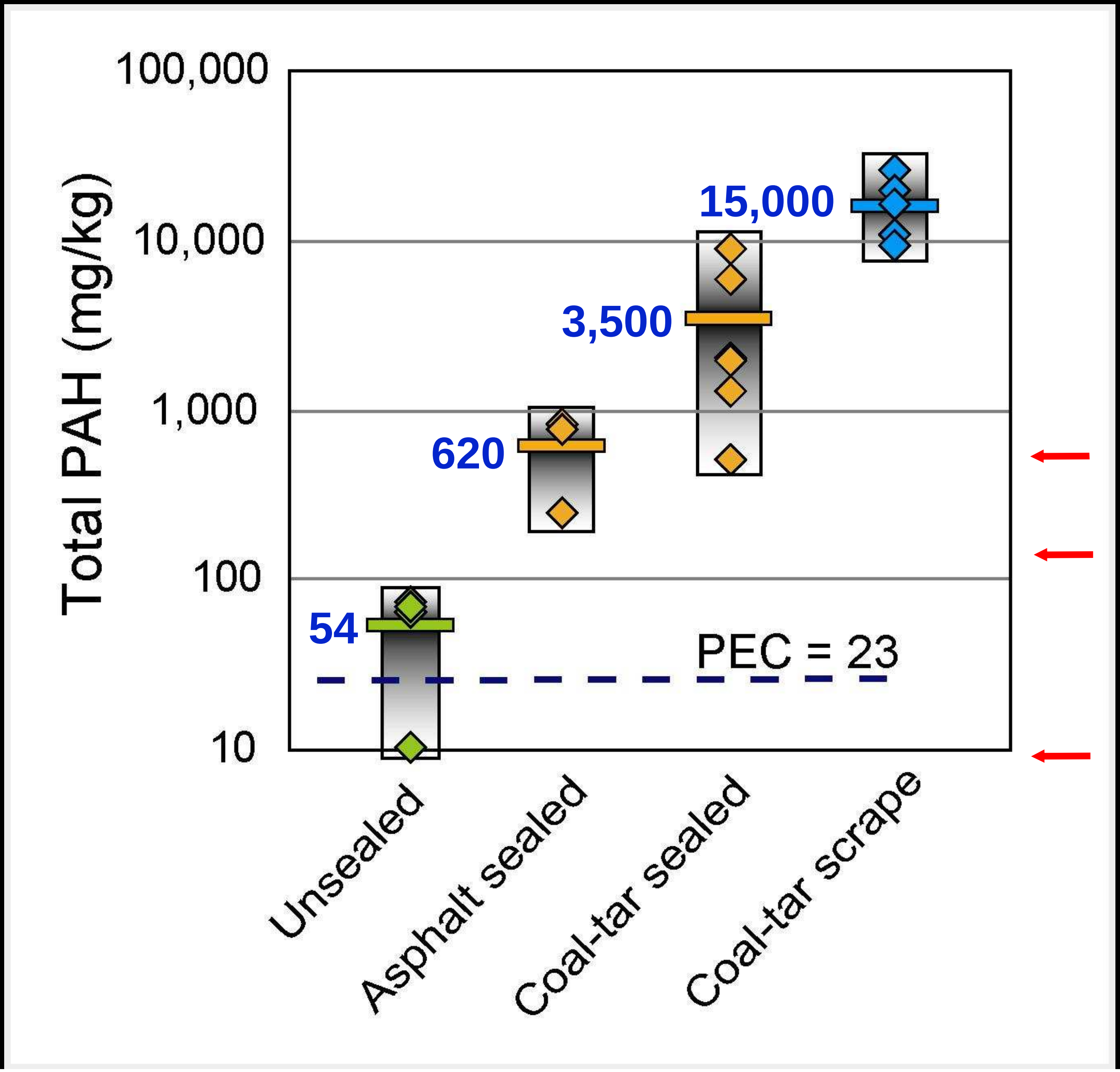


Reilly Site, MN
3,000 max
Black River, OH
1,100

Superfund Sites

Applied over coal-tar-sealcoated pavement

PAHs in Parking Lot Runoff Particles



Used Oil
730 mg/kg

Tires
80-200 mg/kg

Asphalt
2-10 mg/kg

Other urban sources

Environ. Sci. Technol. **2005**, *39*, 5560–5566

Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons

BARBARA J. MAHLER,*,†
PETER C. VAN METRE,†
THOMAS J. BASHARA,‡
JENNIFER T. WILSON,† AND
DAVID A. JOHNS‡

United States Geological Survey, 8027 Exchange Drive, Austin, Texas 78754, and City of Austin Watershed Protection Department, P.O. Box 1088, Austin, Texas 78767

Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous contaminant in urban environments. Although numerous sources of PAHs to urban runoff have been identified, their relative importance remains uncertain. We show that a previously unidentified source of urban PAHs, parking lot sealcoat, may dominate loading of PAHs to urban water bodies in the United States. Particles in runoff from parking lots with coal-tar emulsion sealcoat had mean concentrations of PAHs of 3500 mg/kg, 65 times higher than the mean concentration from unsealed asphalt and cement lots. Diagnostic ratios of individual PAHs indicating sources are similar for particles from coal-tar emulsion sealed lots and suspended sediment from four urban streams. Contaminant yields projected to the watershed scale for the four associated watersheds indicate that runoff from sealed parking lots could account for the majority of stream PAH loads.

Introduction

Concentrations of polycyclic aromatic hydrocarbons (PAHs)—

underlying asphalt pavement and enhance appearance. The two primary sealcoat materials on the market are refined coal-tar-pitch-based emulsion and asphalt-based emulsion. Although similar in appearance (glossy black), coal tar and asphalt have different molecular structures stemming from their origins: coal tar is a byproduct of the production of coke from coal, whereas asphalt is derived from the refining of crude petroleum. Coal tar, a known human carcinogen, is 50% or more PAHs by weight (*2*); the predominant constituents of asphalt are bitumens, complex mixtures of hydrocarbons that include asphaltenes, saturates, aromatics, and resins (*9*). Coal-tar-emulsion- and asphalt-emulsion-based sealcoats typically contain 20–35% of the emulsion.

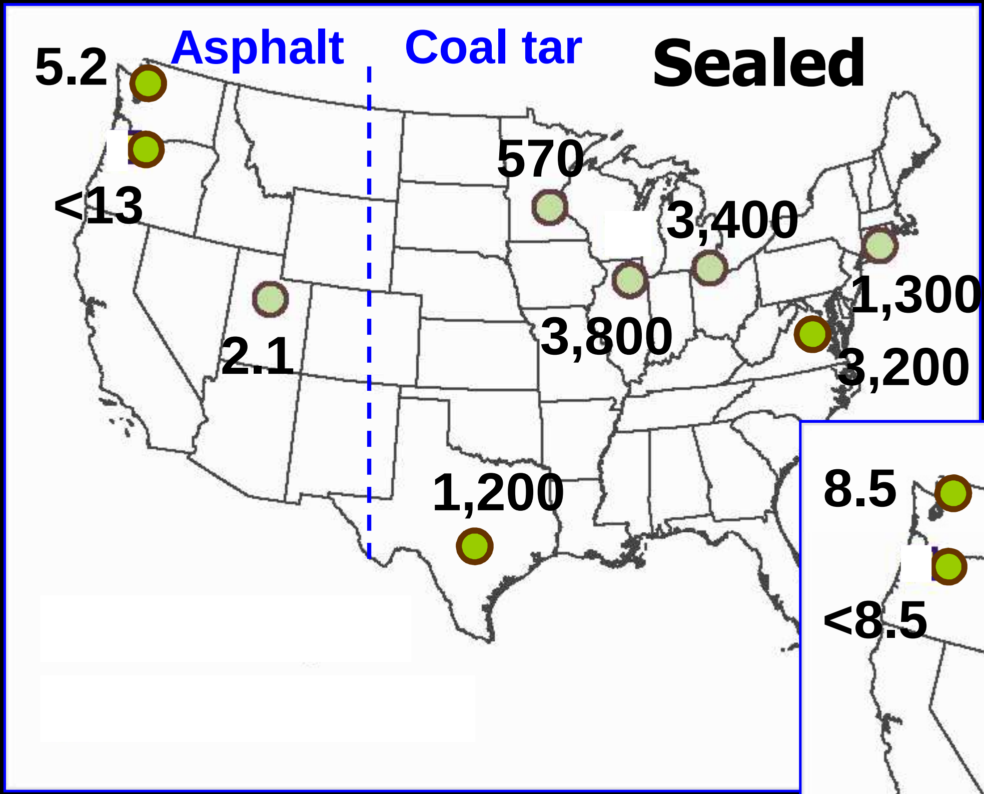
Parking lot sealants are used extensively in the United States and Canada. Although national use figures are not available, the *Blue Book of Building and Construction* (*10*), a directory for the construction industry, lists over 3300 pavement sealant companies in 28 U.S. states. One company advertises the application of 1.7 billion liters to date worldwide (*11*), and another reports having sealed over 33 million square meters (*12*). The City of Austin, population 650000 (2000 census), estimates that about 2.5 million liters of sealcoat is used annually in this city (*13*).

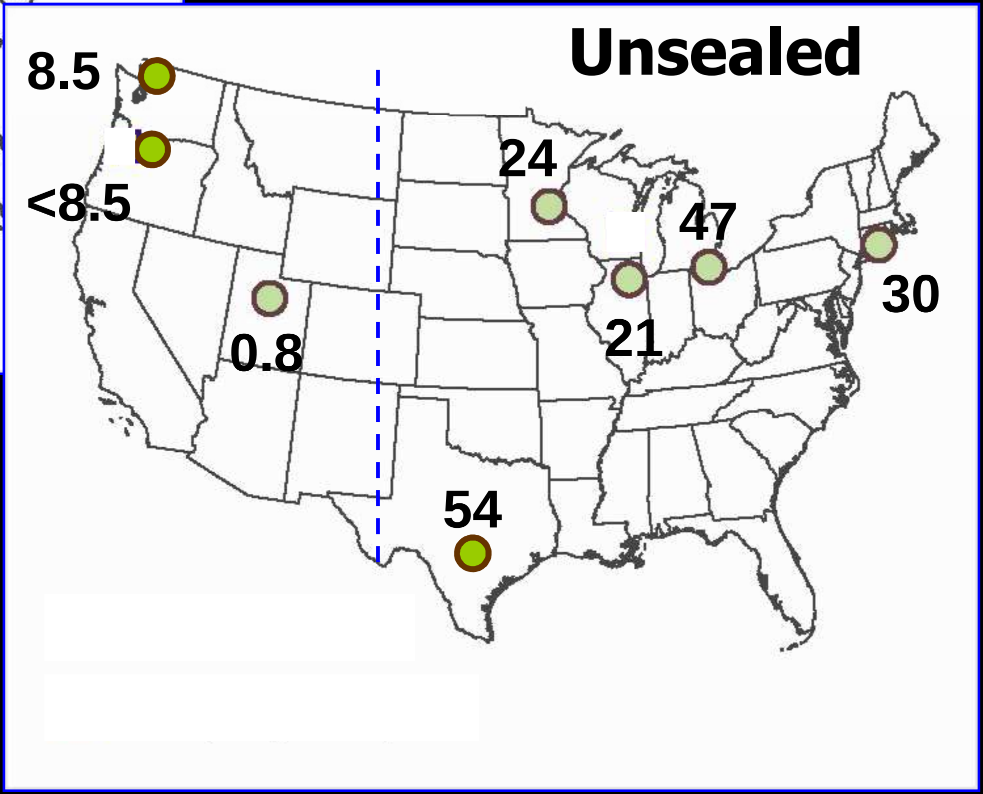
Sealcoat abrades from the parking lot surface relatively rapidly, and reapplication is recommended every two to three years (*14*). In 2003, the City of Austin identified abraded parking lot sealcoat as a possible source of high concentrations of PAHs in streambed sediment (*15*). Here we present evidence suggesting that parking lot sealcoat could indeed be the dominant source of PAHs to watersheds with residential and commercial development.

Experimental Section

Sample Collection. We compared concentrations and yields of particulate PAHs in simulated runoff from parking lots sealed with coal-tar-based sealcoat, from lots sealed with asphalt-based sealcoat, and from unsealed asphalt and cement lots. Thirteen urban parking lots, representing a range of sealant types that are currently in use in Austin, TX, were sampled (Table 1). In addition, four test plots, each about 120 m², were sampled. Three of the test plots were sealed

9 U.S. Cities: Pavement Dust PAH (mg/kg)





Environmental Science and Technology vol. 43, no. 1, 2009.

Research

PAHs Underfoot: Contaminated Dust from Coal-Tar Sealcoated Pavement is Widespread in the United States

PETER C. VAN METRE,*
BARBARA J. MAHLER, AND
JENNIFER T. WILSON
U.S. Geological Survey, Austin, Texas

Received July 29, 2008. Revised manuscript received September 22, 2008. Accepted September 24, 2008.

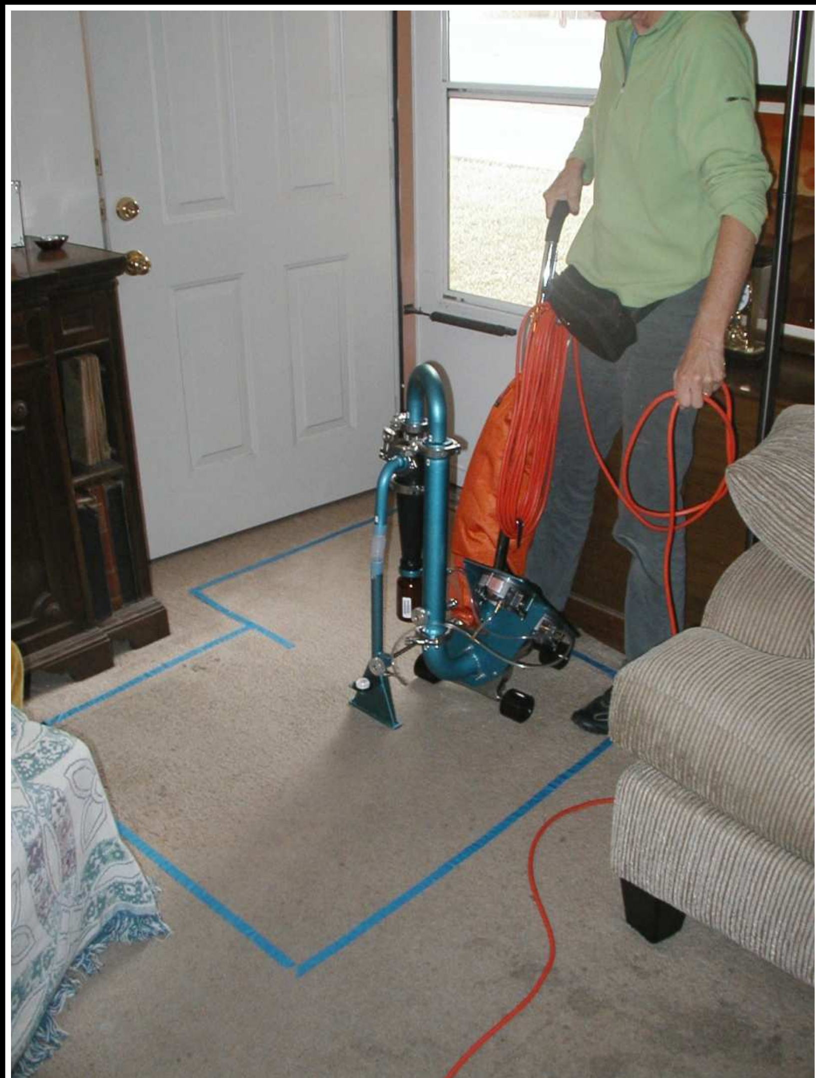
We reported in 2005 that runoff from parking lots treated with coal-tar-based sealcoat was a major source of polycyclic aromatic hydrocarbons (PAHs) to streams in Austin, Texas. Here we present new data from nine U.S. cities that show nationwide patterns in concentrations of PAHs associated with sealcoat. Dust was swept from parking lots in six cities in the central and eastern U.S., where coal-tar-based sealcoat dominates use, and three cities in the western U.S., where asphalt-based sealcoat dominates use. For six central and eastern cities, median ΣPAH concentrations in dust from sealcoated and unsealcoated pavement are 2200 and 27 mg/kg, respectively. For three western cities, median ΣPAH concentrations in dust from sealcoated and unsealcoated pavement are similar and very low (2.1 and 0.8 mg/kg, respectively). Lakes in the central and eastern cities where pavement was sampled have bottom sediments with higher PAH concentrations than do those in the western cities relative to degree of urbanization. Bottom-sediment PAH assemblages are similar to those of sealcoated pavement dust regionally, implicating coal-tar-based sealcoat as a PAH source to the central and eastern lakes

studied. Recent studies have documented adverse biological effects in some Austin streams receiving runoff from coal-tar sealcoated lots (*10*), and demonstrated altered survival, growth, and development in a model amphibian species (*Xenopus laevis*) exposed to sediment spiked with coal-tar-based sealcoat (*11*).

Most sealcoat products have either a refined-coal-tar or asphalt (crude oil) base. The coal-tar varieties typically are 15–35% coal tar, a known carcinogen with extremely high concentrations of PAHs (*12*). The City of Austin reported a median concentration of the sum of 16 PAHs (dry weight basis) for coal-tar-based sealcoat products of more than 50,000 mg/kg and a median for asphalt-based sealcoat products of about 50 mg/kg (*13*). A recent informal survey on the Internet (June 5, 2008) located sealcoat applicators in all 50 U.S. states and Canada (see Supporting Information for Internet sites accessed). Although national use is not reported, the sealcoat industry estimates that in the State of Texas 225 million L of refined coal-tar-based sealcoat are applied annually ((*10*) and references therein), and the New York Academy of Sciences reported estimated annual use of coal-tar-based sealcoat in the New York harbor watershed of approximately 5.3 million L (*14*). Anecdotal reports (e.g., Web sites, blogs, commercial availability, comments by industry representatives) indicate that coal-tar-based sealcoat dominates use east of the Continental Divide (central and eastern U.S) and asphalt-based sealcoat dominates use west of the Continental Divide (western U.S.).

High concentrations of PAHs in particles washed from coal-tar sealcoated parking lots in Austin raise two questions. First, are similarly high PAH concentrations associated with sealcoated pavement in other U.S. cities? Second, does use of coal-tar-based sealcoat lead to contamination of aquatic sediments? To answer these questions, the U.S. Geological Survey (USGS) collected dust from sealcoated and unsealcoated pavement in Austin and eight other U.S. cities; samples were collected in the watersheds of lakes sampled by the USGS National Water-Quality Assessment (NAWQA) Program

23 ground-floor apartments

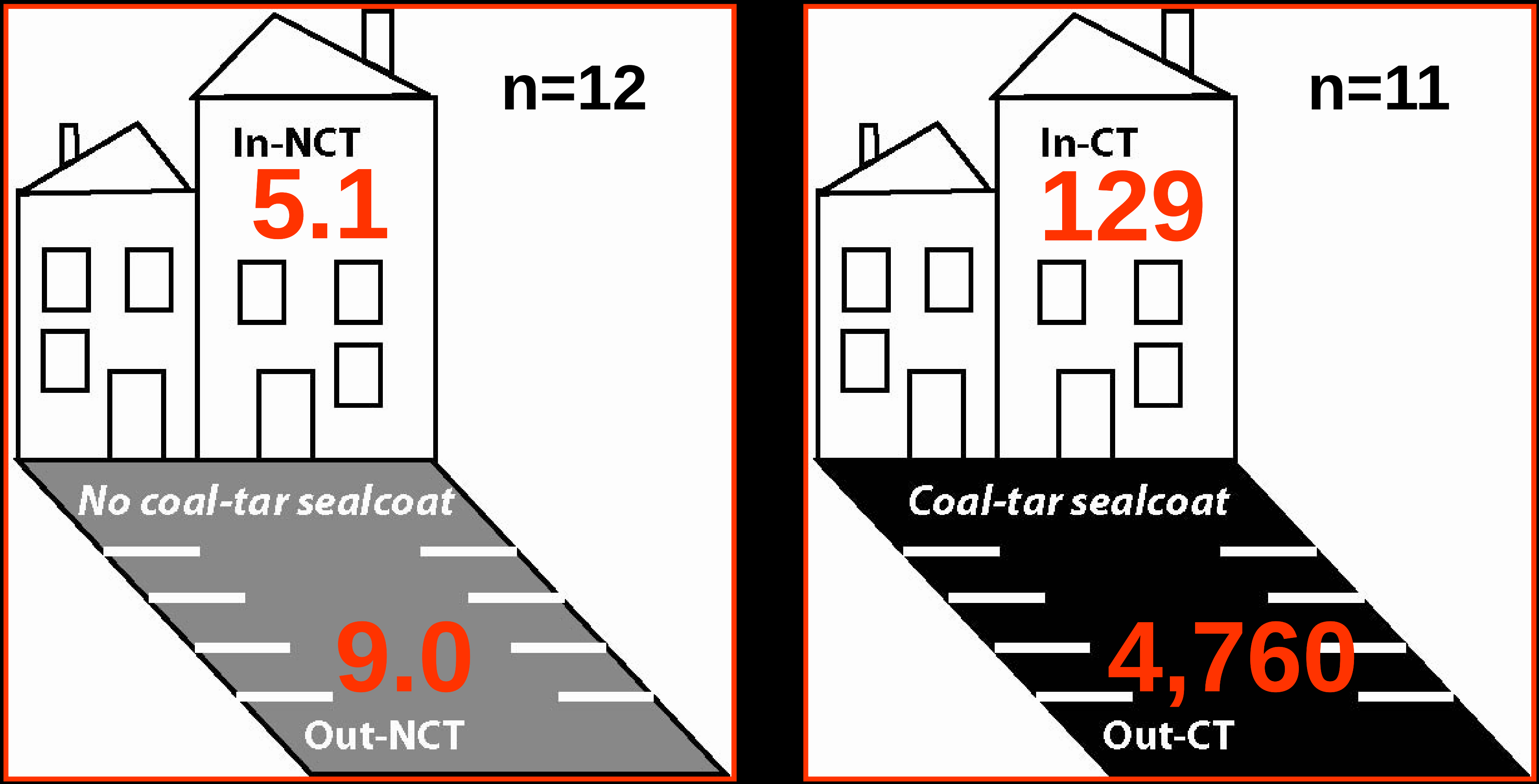


Ancillary Information Gathered

including

- Smoking
- Incense/candles
- Fireplace use
- Type of stove/heat
- Shoe wear in house
- Indoor/outdoor pets
- Distance to major roadway
- Intensity of urbanization

Median total PAH [μg/g]



In-CT = 25 x In-NCT

Out-CT = 530 x Out-NCT

How do pavement dust samples compare?

No coal-tar sealcoat (NCT)

- **15**
- **49**
- **11**
- **4**
- **6**
- **42**
- **8**
- **2**
- **3**
- **17**
- **10**
- **1**

Asphalt-based sealcoat

MEDIAN = 9 μg/g

Coal-tar sealcoat (CT)

- **2,300**
- **10,300**
- **5,070**
- **2,010**
- **591**
- **387**
- **405**
- **11,300**
- **4,760**
- **8,900**
- **6,960**

MEDIAN = 4,760 μg/g

Environ. Sci. Technol. **2010**, *44*, 894–900

Coal-Tar-Based Parking Lot Sealcoat: An Unrecognized Source of PAH to Settled House Dust

BARBARA J. MAHLER,*
PETER C. VAN METRE,
JENNIFER T. WILSON, AND
MARYLYNN MUSGROVE
U.S. Geological Survey, Austin, Texas 78754

TERESA L. BURBANK
U.S. Geological Survey, Denver, Colorado 80225

THOMAS E. ENNIS
Designs4Earth, Inc., P.O. Box 373, Manchaca, Texas 78652

THOMAS J. BASHARA
Watershed Protection Department, City of Austin, Austin, Texas 78701

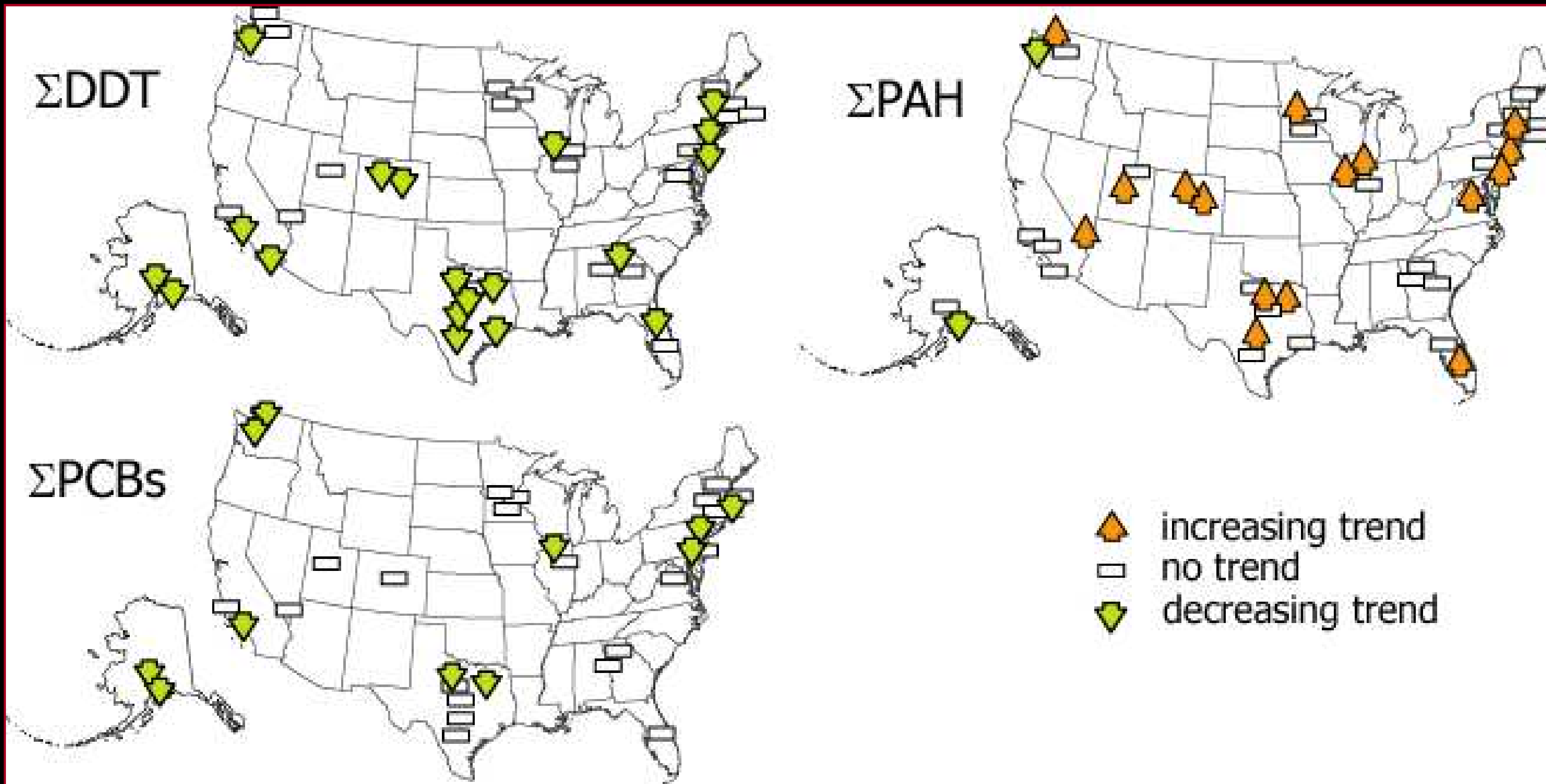
Received August 19, 2009. Revised manuscript received December 1, 2009. Accepted December 3, 2009.

Despite much speculation, the principal factors controlling concentrations of polycyclic aromatic hydrocarbons (PAH) in settled house dust (SHD) have not yet been identified. In response to recent reports that dust from pavement with coal-tar-based sealcoat contains extremely high concentrations of PAH, we measured PAH in SHD from 23 apartments and in dust from their associated parking lots, one-half of which had coal-tar-based sealcoat (CT). The median concentration of total PAH (T-PAH) in dust from CT parking lots (4760 μg/g, $n = 11$) was 530 times higher than that from parking lots with

There are numerous potential indoor and outdoor sources of PAHs to SHD, which is a complex mixture of biological material, particulate deposition of indoor aerosols, and particles tracked in from the outdoors (*14*). PAHs are formed during the incomplete combustion of carbonaceous material, including wood, coal, food, motor oil, and gasoline. Researchers, however, have remarked on the lack of success in identifying the principal sources contributing to the PAH content of SHD (*1, 9*). Maertens et al. (*9*) compiled data for PAH composition and concentrations in SHD from 18 published studies and investigated relations between PAHs and numerous site attributes and lifestyle variables. They determined that only tobacco smoking (significant in urban homes only) and home location (urban vs rural) were related to PAH content, and that the relations were weak. The significance of tobacco smoking as a factor affecting PAH concentrations has been corroborated by some studies (*10, 12, 15*) but not by others (*5, 11*). At least one other study (*12*) found that rural areas had lower concentrations of PAHs in SHD than did urban areas, although only two samples from rural areas were analyzed. Other factors, such as heating with coal (*10*), vehicle emissions (*10*), and carpeting (*11*), cited as potential explanatory variables for differences in PAH concentrations, have not been demonstrated to be significant.

A recently identified outdoor source of PAHs to the environment (*16, 17*)—coal-tar-based pavement sealcoat—has not been considered in any previous investigations of PAHs in SHD. Sealcoat is the black liquid that is sprayed or painted on the asphalt pavement of many parking lots, driveways, and playgrounds in the U.S. and Canada in an attempt to improve appearance and increase pavement longevity. There are two principal formulations of sealcoat: one with a refined coal-tar-emulsion (RT-12 grade) base and one with an asphalt-emulsion base. Coal tar is a known carcinogen that is more than 50% PAH by weight (*18*); sealcoat with a coal-tar base typically is 15 to 35% refined coal tar. The median PAH concentration (sum of 16 parent PAHs) for coal-tar-based and asphalt-based sealcoat products has been reported

Increasing trends in PAHs

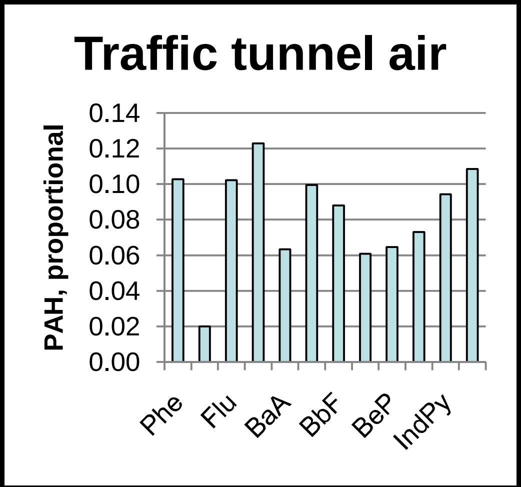


Van Metre and Mahler, 2005, Environmental Sci. & Tech.

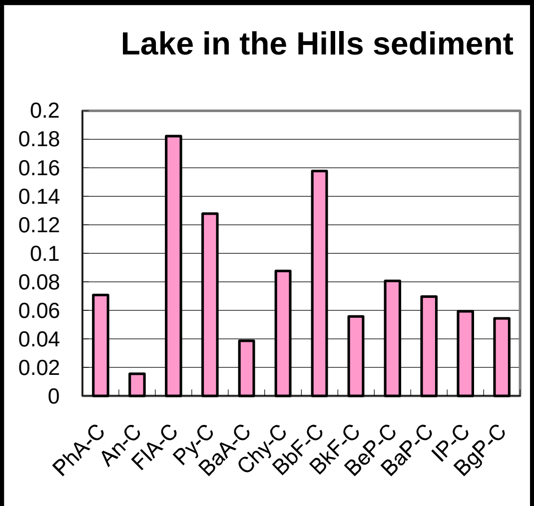
"Contribution of PAHs from Coal-Tar Pavement Sealcoat and Other Sources to 40 U.S. Lakes" (Submitted to *Science of the Total Environment*)

- Start with source profiles and receptor profiles
- CMB combines sources to best match the receptor profile
- Results are the contribution of each source to each sediment sample

Example source



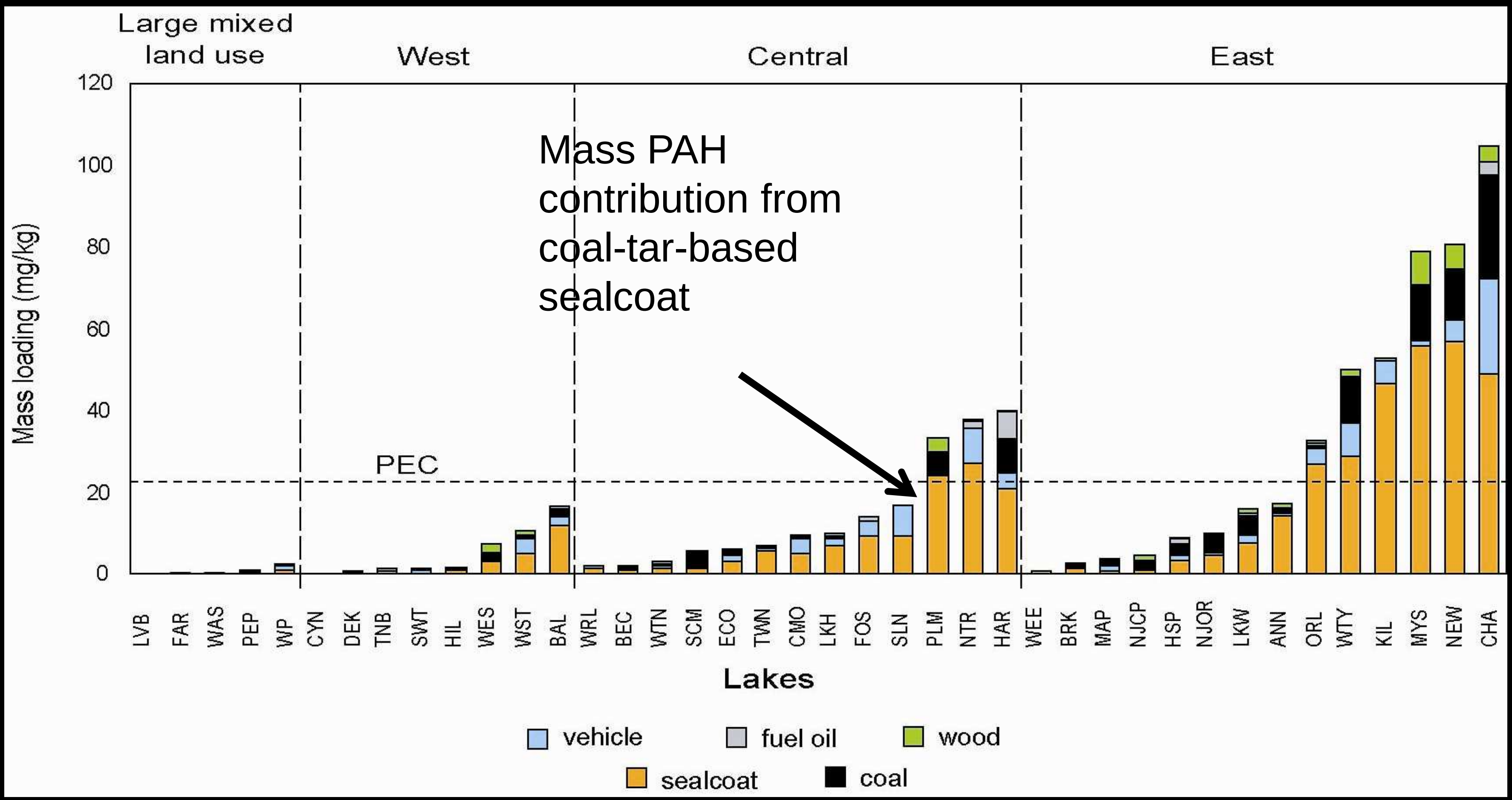
Example receptor



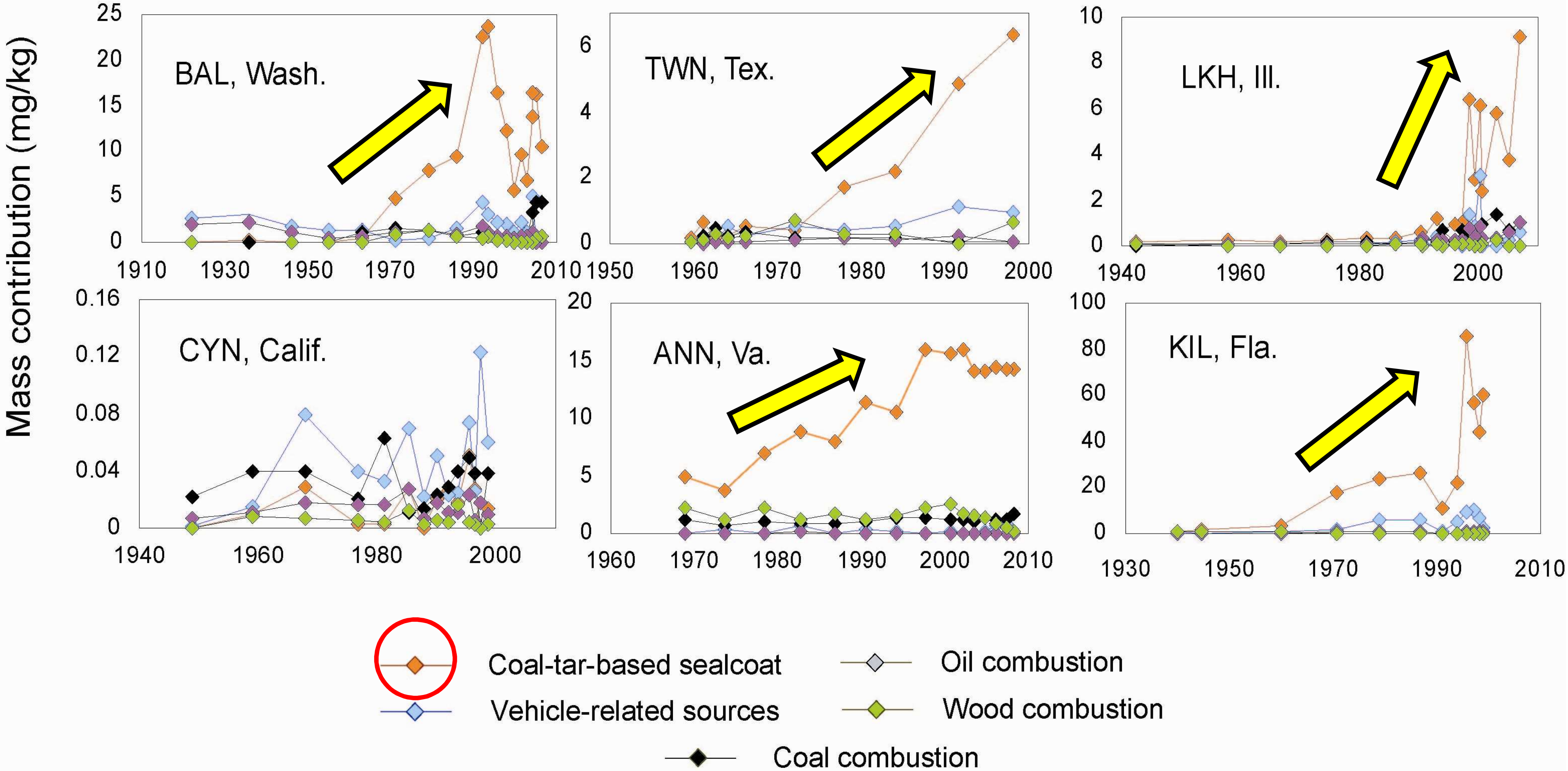
Sources Considered

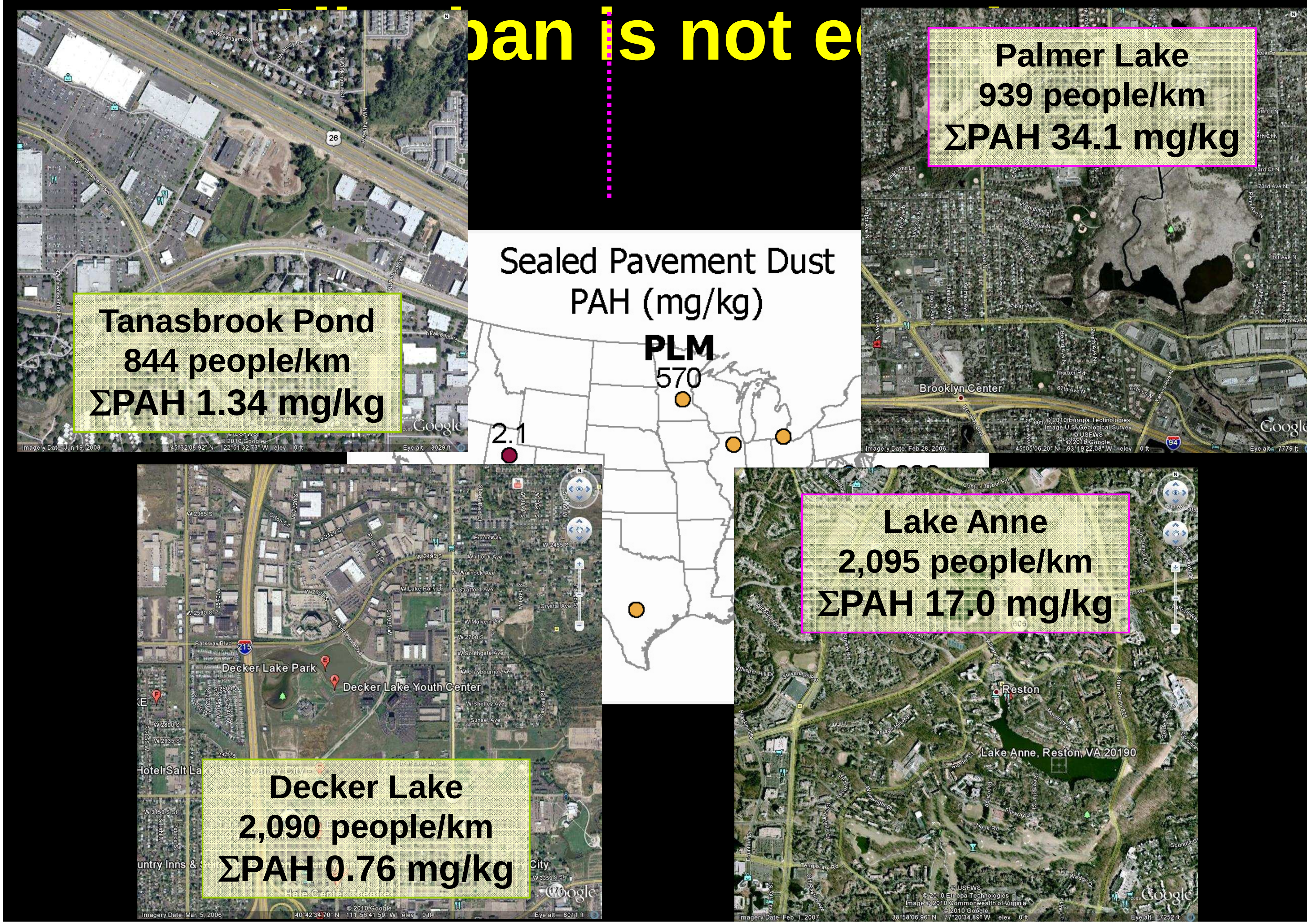
- Coal combustion
  - Power plant emissions
  - Residential heating
  - Coke oven
- Vehicle related
  - Diesel vehicle emissions
  - Gasoline vehicle emissions
  - Traffic tunnel air
  - Used motor oil
  - Tire particles
  - Asphalt
- Fuel-oil combustion
- Wood burning
  - Pine-wood soot particles
- Coal-tar-sealcoat related
  - NIST coal tar standard
  - Sealcoat products
  - Sealcoat scrapings
  - Sealcoat dust (average, 6 cities)
  - Sealcoat dust, Austin

PAH Source Apportionment to 40 U.S. Lakes



PAH Trends in New Urban Lakes




ban is not e
Tanasbrook Pond
844 people/km
ΣPAH 1.34 mg/kg
Palmer Lake
939 people/km
ΣPAH 34.1 mg/kg
Sealed Pavement Dust
PAH (mg/kg)
PLM
570
2.1
Brooklyn Center
Decker Lake Park
Decker Lake Youth Center
Decker Lake
2,090 people/km
ΣPAH 0.76 mg/kg
Lake Anne
2,095 people/km
ΣPAH 17.0 mg/kg
Reston
Lake Anne, Reston, VA 20190


PAHs are increasing in urban lakes nationally
Coal-tar-based sealcoat has exceptionally high PAH concentrations, particles are mobile, and use is extensive
PAHs in house dust are elevated where coal-tar-based sealcoat is used
Coal-tar-based sealcoat is the largest contributor of PAHs to urban lakes
8/31/2000